ITN Energy Systems, Inc.
8130 Shaffer Parkway, Littleton, Colorado 80127-4107

Voice: 303 420 1141 | Fax: 303 420 1551
Email: info@itnes.com | Web: www.itnes.com

June 17, 2004

Dr. Harin Ullal, MS3212
National Center for Photovoltaics
National Renewable Energy Laboratory
1617 Cole Blvd
Golden, CO 80401

Re: Thirtieth Monthly Report #NDJ-2-30630-11

Dear Harin,

This letter comprises the monthly technical status report for ITN's subcontract # NDJ-2-30630-11, "Plasma-Assisted Coevaporation of S and Se for Wide Band Gap Chalcopyrite Photovoltaics", under the Thin Film Partnership Program. The reported work was performed during the sixth month of phase 3 for this contract (thirtieth month overall), which is May 7, 2004 through June 7, 2004. This report describes activities performed by ITN, as well as those performed by lower-tier subcontractor Colorado School of Mines (CSM), under the direction of Dr. Colin Wolden.

1. Program Goals and Approach

Our primary objective under this program is to determine if the chalcogen in CIGS co-evaporation can be delivered more effectively by activation with a plasma. Possible advantages of plasma-assisted co-evaporation (PACE) are

- increased utilization of chalcogens,
- decreased deposition temperatures,
- decreased deposition times, and
- increased ability to tailor S/Se ratio.

University researchers at CSM are developing and testing the fundamental chemistry and engineering principles. Industrial researchers at ITN are adapting PACE technology to CIGSS co-evaporation and validating PACE process for fabrication of thin film PV. In_2Se_3 films, which are used as precursor layers in high-efficiency CIGS depositions, were used as the first test case for the examining the advantages of PACE listed above, and significant advantages were demonstrated. Presently, the examination is being extended to the complete high-efficiency three-stage CIGS co-evaporation process.

2. Incorporation of PACE Sources Into Three-Stage Deposition

This month, important progress toward full incorporation of PACE processing into three-stage CIGS deposition was made. First, the PACE source was operated during several three-stage CIGS depositions. (RF was not applied during these tests.) Rate, control, and uniformity continue to be adequate. CIGS films were formed into devices, and it was verified that device performance is unchanged by substituting the PACE source (without RF) for the traditional tantalum evaporation baffled box. Second, modifications to control hardware to allow routine and automatic usage of the PACE source (rather than the tantalum boat) were planned out. Third, several steps were taken toward full installation of RF in the three-stage CIGS chamber. The RF power supply and network were mounted in the chamber electrical cabinet, including the necessary 280V supply and increased cabinet cooling. Several components on the chamber that would physically obstruct the RF were relocated, including vacuum gauges, Eurotherms, and the emergency stop button.

3. Demonstrating Advantages of PACE

A key anticipated benefit of PACE is the reduction of CIGS deposition temperatures. To demonstrate this advantage, CIGS will be deposited at reduced temperatures known[1,2] to be detrimental to device efficiency. Some depositions will be performed with plasma-activation of the chalcogen, and others without. Device performance will be compared. As a first step in this comparison, several CIGS films were deposited at 400 ^{o}C this month, without plasma activation. These films are currently being finished into devices.

4. Plasma-Assisted Film Kinetics

It was demonstrated last month in the CSM benchtop source that, for conditions explored to date, the formation of CIS and CIGS at 300 ^{o}C utilizing plasma-activated Se is limited by mass transport (i.e. total Se exposure), not film formation kinetics (e.g. temperature). This month, work was performed to expand upon that result. This work included an examination of film microstructure, fabrication of a control film without plasma, and experiments with larger Se flux.

Figure 1 shows XRD patterns and corresponding ESEM micrographs of films that experienced (a) poor conversion, (b) partial conversion, or (c) full conversion to CIGS, as discerned last month by XRD. The first sample, (A), is characterized by an XRD pattern in which the initial indium peaks have disappeared, but there is little crystalline chalcopyrite formation. The ESEM image shows a surface with few distinguishing features. In sample (B), XRD yields clear evidenced of both CIS and CGS ternary phases, but not CIGS. The

[1] M. Lammer, U. Klemm, M. Powalla, "Sodium co-evaporation for low temperature Cu(In,Ga)Se2 deposition," *Thin Solid Films* **387**, (2001), pp. 33-36.
[2] W.N. Shafarman, J. Zhu, "Effect of Grain Size, Morphology, and Deposition Temperature on Cu(InGa)Se_2 Solar Cells," *Materials Research Society Symposium Proceedings* **668**, (2001), pp. H2.3.1-H2.3.6.

morphology is characterized by two types features: one that appears lighter and with a fibrous texture, while another that appears smooth and darker. Using EDS, no Ga is detected on the white features, while Ga is present in the darker features. The third sample, (C), is characterized by XRD peaks whose positions correspond to the quaternary CIGS alloy. The morphology is that of a more distinct, polycrystalline sample. EDS spectra measured at different spots around the sample were compositionally uniform, with Ga present at each location.

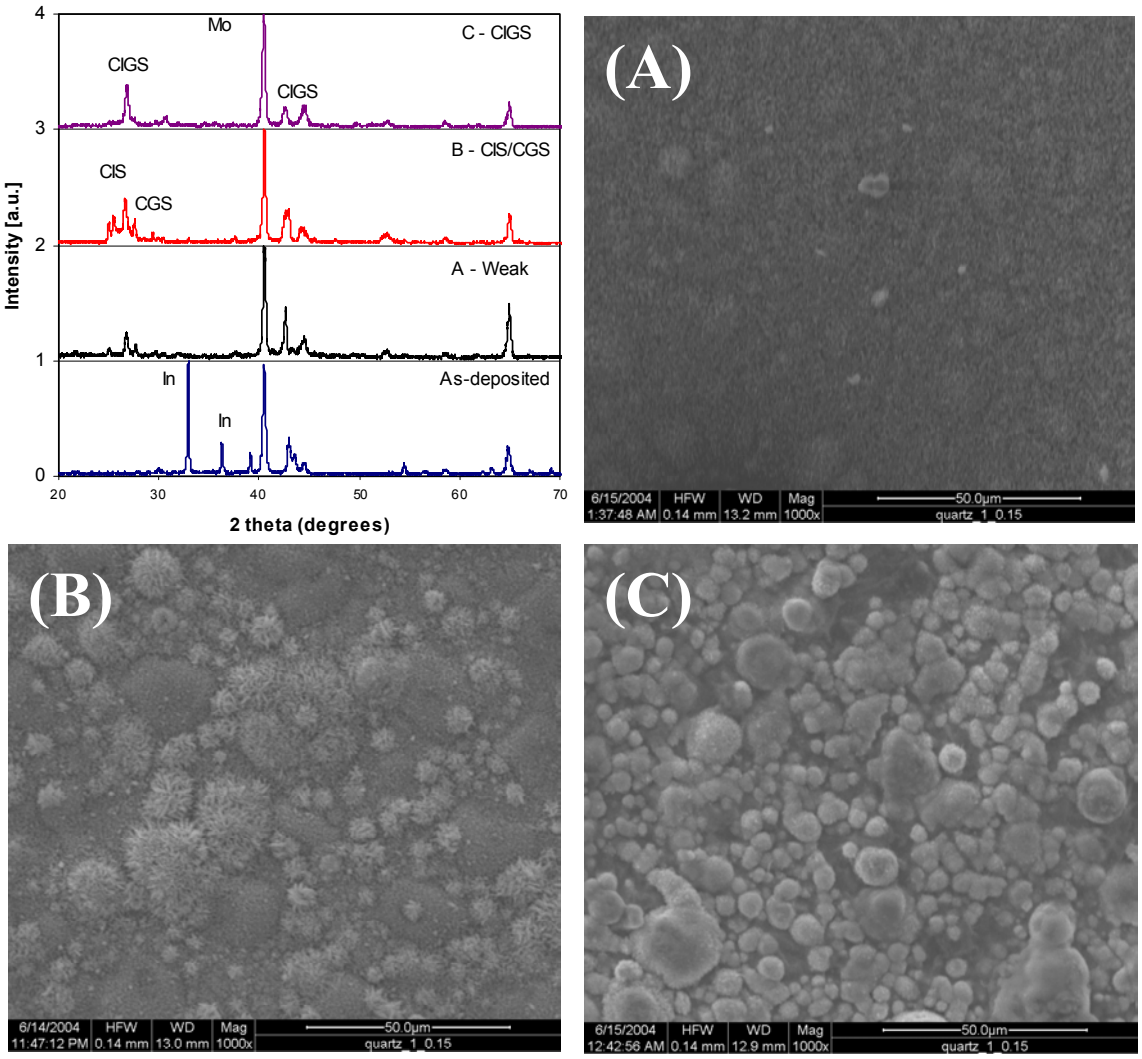


Figure 1: XRD patterns and corresponding micrographs.

The main difference between the samples (A)-(C) was the amount of selenium exposure. Additional experiments were attempted in the benchtop source with increased amounts of Se. However the flux was difficult to control, and the ICP tube became coated with Se. Under these conditions, a plasma cannot be maintained. For more precise control of chalcogen flux, particularly at high rates, plumbing has been installed to the benchtop source for utilization of H_2S. The primary advantage is that the chalcogen density can be precisely controlled by setting flow rates and pressure. The CSM environmental health and safety office is installing a H_2S

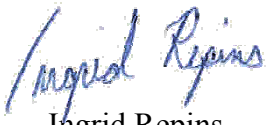
detector, that will be interfaced with automatic shut off valves for safety. Moreover, a 10% H_2S mixture diluted will be used to further mitigate safety concerns.

To clearly demonstrate the advantage of plasma-activation for CIGS formation, an additional experiment was performed exposing the heated sample to a high flux of selenium at 300 ^{o}C, without plasma. The XRD patterns showed little or no evidence of chalcopyrite phases (CIS, CGS, or CIGS).

5. Team Activities

ITN and CSM participate in CIS team activities. Last month, an outline of a publication describing absorber sub-team activities was distributed for review to contributors. This month the outline was slightly revised according to participant comments.

Best Wishes,



Ingrid Repins
Principal investigator
ITN Energy Systems

Cc: Ms. Carolyn Lopez; NREL contracts and business services
Dr. Colin Wolden; CSM technical lead